



## IDENTIFICACION DE FUENTES POTENCIALES DE LITIO EN LAS SALMUERAS PROFUNDAS DEL SALAR DE OLARAZ MEDIANTE ANALISIS GEOQUÍMICOS E ISOTÓPICOS

### IDENTIFICATION OF POTENTIAL SOURCES OF LITHIUM IN DEEP BRINES OF THE OLARAZ SALAR USING A GEOCHEMICAL AND ISOTOPIC APPROACH

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#### Abstract

*The salar de Olaroz is the main Li project in Argentina but the sources and dynamics of the element in this basin are still unknown. In order to identify sources and to understand the dynamics of Li in the salt pan, chemical and isotopic analysis ( $\delta^7\text{Li}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) of brines, thermal waters, ignimbrites and sediments outcropping in the basin were performed. The results indicate that the origin of the Li present in the brines is the result of bedrock weathering (likely volcanoclastic sediments and ignimbrites), enhanced by warm thermal waters circulating at depth. An important fraction of Li is likely adsorbed onto clay minerals and Fe (hydr)oxides present in deep fine-grained sediments. Therefore, it is expected that high concentrations of Li are also found in sediments.*

**Key words:** *ignimbrites, weathering,  $\delta^7\text{Li}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ , thermal springs.*

#### Introduction

The world's largest lithium-bearing evaporite basins are in the Puna Plateau, where several hydroclimatic and geological factors converge to develop lithium-rich brine deposits (Munk et al., 2016). One of the most recent operations in the northern Puna region of Argentina is emplaced in the Salar de Olaroz, where the company Sales de Jujuy produces Li carbonate.

The Salar de Olaroz is a 130 km<sup>2</sup> salt pan fed by two main rivers. The Rosario River is the main fluvial system. It discharges in the northern part of the salt pan (Fig. 1), where it forms a large alluvial fan with numerous springs of geothermal water with outlet temperatures lower than 30°C (Peralta Arnold et al., 2017). The other main tributary to the salar is the Archibarca River that reaches the salt pan from the South-west (López Steinmetz et al., 2018).

The main units in the study area consist of Lower to Middle Ordovician (Santa Victoria Group) metasedimentary rocks that outcrop in the ranges that confine the salar; Cretaceous to Palaeocene rift-related sedimentary rocks (Salta Group); Upper Eocene to Middle to Upper Miocene synorogenic red beds; Middle to Upper Miocene fluvial to lacustrine units with intercalated air fall tuffs and pyroclastic flow deposits (Tiomayo, Trincheras and Pastos Chicos Formations); Upper Miocene-Pliocene sedimentary/volcanoclastic deposits (Loma Blanca/Sijes Formations) which are also recording the onset of evaporative systems. Widespread Upper Miocene-Pliocene and Pleistocene ignimbrites cover large areas of the basin catchments. Quaternary alluvial fans extend between the foot of the mountains and the low-lying flat areas, which are in turn covered by fine-grained lacustrine sediments and salt pans.

Although felsic volcanic rocks such as ignimbrites and volcanic-related hydrothermal activity have been considered the main sources of Li to Andean salars (Lowenstein and Risacher 2009), there is still little geochemical information about the bulk Li concentrations in such volcanic rocks and thermal waters. Thus, the sources of Li in the brines hosted at the salar de Olaroz remain still unknown. Contributions of Li from rock weathering can be assessed using the  $^7\text{Li}/^6\text{Li}$  ratio because  $^6\text{Li}$  partitions preferentially into secondary minerals formed during

chemical weathering of silicate rocks (e.g., clays and oxides/hydroxides), while  $^7\text{Li}$  partitions preferentially into the associated water (i.e., Pogge von Strandmann et al. 2010).  $\delta^7\text{Li}$  values can be also a valuable tool to trace Li contributions from geothermal water inputs (Penniston-Dorland et al., 2017).



Figure 1. Study area and location of sampling points

Only a few data of Li isotopes in the Puna's waters and brines are available. For example, Godfrey et al. (2013) inferred Li contributions to the Hombre Muerto salar's brines (Southern Puna of Argentina) from geothermal waters that likely recharge the main river discharging into the salar, as the low  $\delta^7\text{Li}$  values ( $\delta^7\text{Li} = +3.4\text{‰}$ ) measured in the river are compatible with a hydrothermal source of Li. In addition, these authors conclude that Li is physi-sorbed into clay minerals during the transport from the sources until its final accumulation in the brines. More recently, Rojas and Alonso (2018) reported  $\delta^7\text{Li}$  values for the shallow and deep brines of the Ratones and Centenario salars (southern Puna) that averaged  $+9.2$  and  $+9.7\text{‰}$  respectively. Based on the Li and stable water isotopes signatures, the authors propose that the main contribution of Li to these salars is related to the interaction of surface saline waters with regional rocks such as andesites, pegmatites and pyroclastic deposits.

Even though the Olaroz salar is currently the most important Li mine in Argentina, the sources and dynamics of Li in the basin are still unknown. Therefore, the main goal of this work is to analyse the Li isotope signatures of deep and shallow brines as well as freshwater discharging into the salar de Olaroz in order to identify potential sources and to define the geochemical processes that control its distribution between the aqueous and mineral phases within the aquifers.

### Materials and Methods

Shallow brines were collected from ~60 cm deep pits dug along two transects located in the northern and central part of the salar nucleus in April 2016, while deep brines (150-450 m b.s.) were collected in May 2018 from the network of exploitation boreholes drilled by the mining company. Samples of the Archibarca and Rosario Rivers were collected a few kilometres upstream of where they discharge into de salar during both sampling campaigns. Other water samples were collected from shallow lakes and outlets of thermal water located in the northern margin of the salar nucleus (Fig. 1). Samples of the Toro and Coranzulí ignimbrites were collected from outcrops located in the northern part of the salar, while samples of the Sijes and Trincheras formations were collected in the southern and western border of the salar.

The chemical composition of brines and rocks was measured by ICP-MS (ThermoScientific iCap-Q) at Rutgers University, after multi-acid digestion ( $\text{HNO}_3 + \text{HCl} + \text{HF}$ ). Lithium and strontium



isotopes were also analysed at Rutgers University, using a ThermoScientific Neptune Plus multicollector ICP-MS (MC ICP-MS). Li was separated from other constituents in a two-stage column process using cation resin AG50W-X12 and 0.5N HCl. Samples were checked to insure quantitative Li recovery and separation from Na before analysis; seawater was also analysed to further check on column and instrument performance. Lithium isotope analyses followed the standard-bracketing method once signal intensities were matched to the bracketing standard to within 5%. Isotope data are reported as  $\delta^7\text{Li}$  in ‰ units relative to NIST standard L-SVEC, where:

$$\delta^7\text{Li} = [((^7\text{Li}/^6\text{Li})_{\text{muestra}} - (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}) / (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}}] * 1000$$

Strontium determinations were carried out using a ThermoScientific Neptune Plus multicollector ICP-MS following extraction using Sr-specific resin (Eichrom). NIST 987 run during analysis periods was  $0.710270 \pm 10\text{ppm}$  (2SD,  $n=12$ ).

## Results

Shallow and deep brines in Olaroz are a Na-Chloride type which is typical of mature brines in equilibrium with halite and mirabilite. Lithium concentrations in the shallow brines (average:  $649 \text{ mg L}^{-1}$ ) are lower than those determined in deep brines (average:  $993 \text{ mg L}^{-1}$ ). The spatial distribution of the Li concentrations reveals that concentrations higher than  $700 \text{ mg L}^{-1}$  are in the centre and northern part of the salt flat nucleus. As expected, Li concentrations in river waters feeding the salar are low ( $< 5 \text{ mg L}^{-1}$ ), while in the shallow lakes located on the Rosario River alluvial fan, Li concentrations range from 38 to  $167 \text{ mg L}^{-1}$ . In this area, springs of thermal waters have Li concentrations that varied with time:  $2 \text{ mg L}^{-1}$  in 2016 and  $40 \text{ mg L}^{-1}$  in 2018, with no evident relation with climate or hydrologic conditions.

Strontium concentrations range from  $9.7$  to  $86 \text{ mg L}^{-1}$  in deep brines while in shallow brines concentrations reach up to  $\sim 150 \text{ mg L}^{-1}$ . Surficial waters show more variable Sr concentrations ranging from 0.5 (Archibarca River) to  $57 \text{ mg L}^{-1}$  (Rosario River). The  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  diagram (Fig. 2a) shows that  $^{87}\text{Sr}/^{86}\text{Sr}$  range for shallow and deep brines is 0.713–0.715, and 0.715–0.717 for surficial waters and thermal waters of the northern part of the salt pan. These signatures are characteristic of waters draining felsic terrains (e.g., Négrel et al., 2000). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio of the Archibarca River and the groundwater sample pumped from the river's alluvial fan is  $\sim 0.711$ , indicating a different, less radiogenic, rock source for these waters.

The Li isotopic compositions of deep brines are the highest with  $\delta^7\text{Li}$  values ranging from +8.09 to +10.20 ‰. The lowest Li isotopic signature was determined in the Rosario River ( $\delta^7\text{Li} = +2.1$  ‰), which suggests contributions from thermal waters into this river. Interestingly, the  $\delta^7\text{Li}$  values registered in thermal springs are slightly higher, with an average value of +5.7 ‰. The  $\delta^7\text{Li}$  of the Archibarca River is +7.6 ‰, which is slightly higher than the  $\delta^7\text{Li}$  values determined in shallow brines (from +5.9 to +7.2 ‰) and reveals that the Li-supplying role of this river is minor since it is isotopically more evolved than the shallow brines with which it mixes.

The Sr isotopic ratios of the Toro and Coranzulí ignimbrites are 0.71211 and 0.712084 respectively, while the corresponding ratios in the Sijes and Trinchera Fms are in the range 0.712–0.715, and 0.711–0.716 respectively. Interestingly, the most radiogenic values were determined in tuff layers of the Sijes Fm and in the uppermost layer of the Trinchera Fm (both, tuff and volcanoclastic layers). The Li concentrations vary from 60 to  $90 \text{ mg Kg}^{-1}$  in ignimbrites to  $\sim 25 \text{ mg Kg}^{-1}$  in the Trinchera Fm. In volcanic ashes the concentration of Li averages  $44 \text{ mg Kg}^{-1}$ . The  $\delta^7\text{Li}$  values of most of the rocks and sediments samples are negative or near 0 and vary between -13.8 and +0.5‰.

Figure 2 b shows the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio against  $\delta^7\text{Li}$  of water and rock samples of Olaroz. This figure reveals that the chemical composition of brines in Olaroz is the result of mixing between supplies that are being sourced from bedrock weathering (likely ignimbrites and volcanic ashes) and minor hydrothermal contributions. The radiogenic nature of thermal waters in the study area, also suggests that solutes in these waters are the result of weathering of deeper felsic rocks enhanced by temperature. Once these meteoric and thermal waters reach the salar, a significant increase in Li concentrations occurs due to evaporation. This process produces no Li isotopic fractionation, which explains the nearly constant values of  $\delta^7\text{Li}$  found in the brines.

Higher  $\delta^7\text{Li}$  determined in deep brines are likely the result of the preferential adsorption of  $^6\text{Li}$  onto clays and Fe(oxy)hydroxides minerals due to a longer residence time in deeper aquifers and prolonged water/sediment interaction.

## Conclusions

The isotopic and chemical signatures of shallow and deep brines occupying the Olaroz salar suggest that the Li accumulating in the salar results from bedrock weathering (predominantly volcanoclastic sediments and ignimbrites), enhanced by warm thermal waters circulating at depth. Within the salt pan, Li concentrations increase by two or three orders of magnitude when compared with the values determined in the main tributaries and outlets of thermal waters due to evaporation. Deeper in the salt pan, where fine grain-size sediments occur, isotopes indicate that an important component of the Li has been adsorbed onto clay minerals and Fe (hydr)oxides. Consequently, high concentrations of Li might be stored in sediments accumulated below the salt crust.

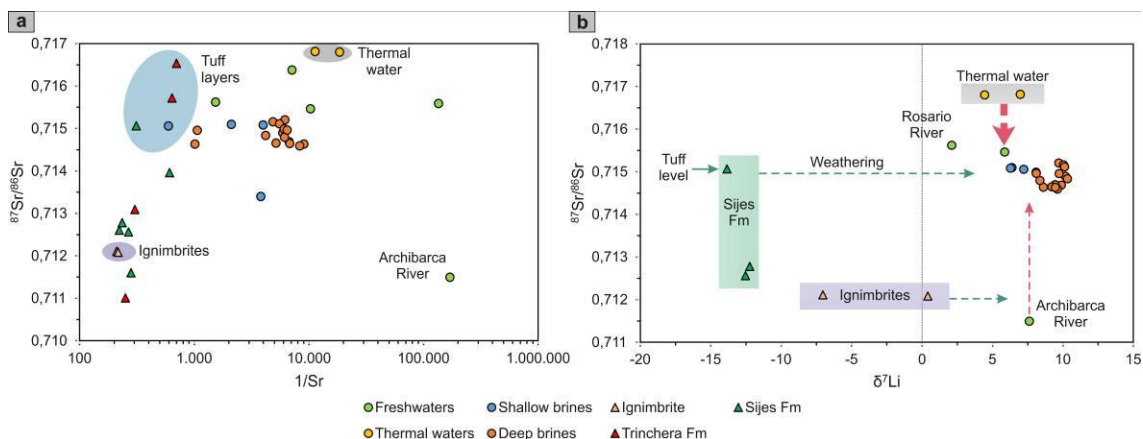


Figure 2. a) Strontium isotopic ratios plotted vs. the inverse of Sr concentration and b) Sr isotopic ratios plotted vs. Li isotopes in brines and rocks from the Salar de Olaroz

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